FIG. 1A

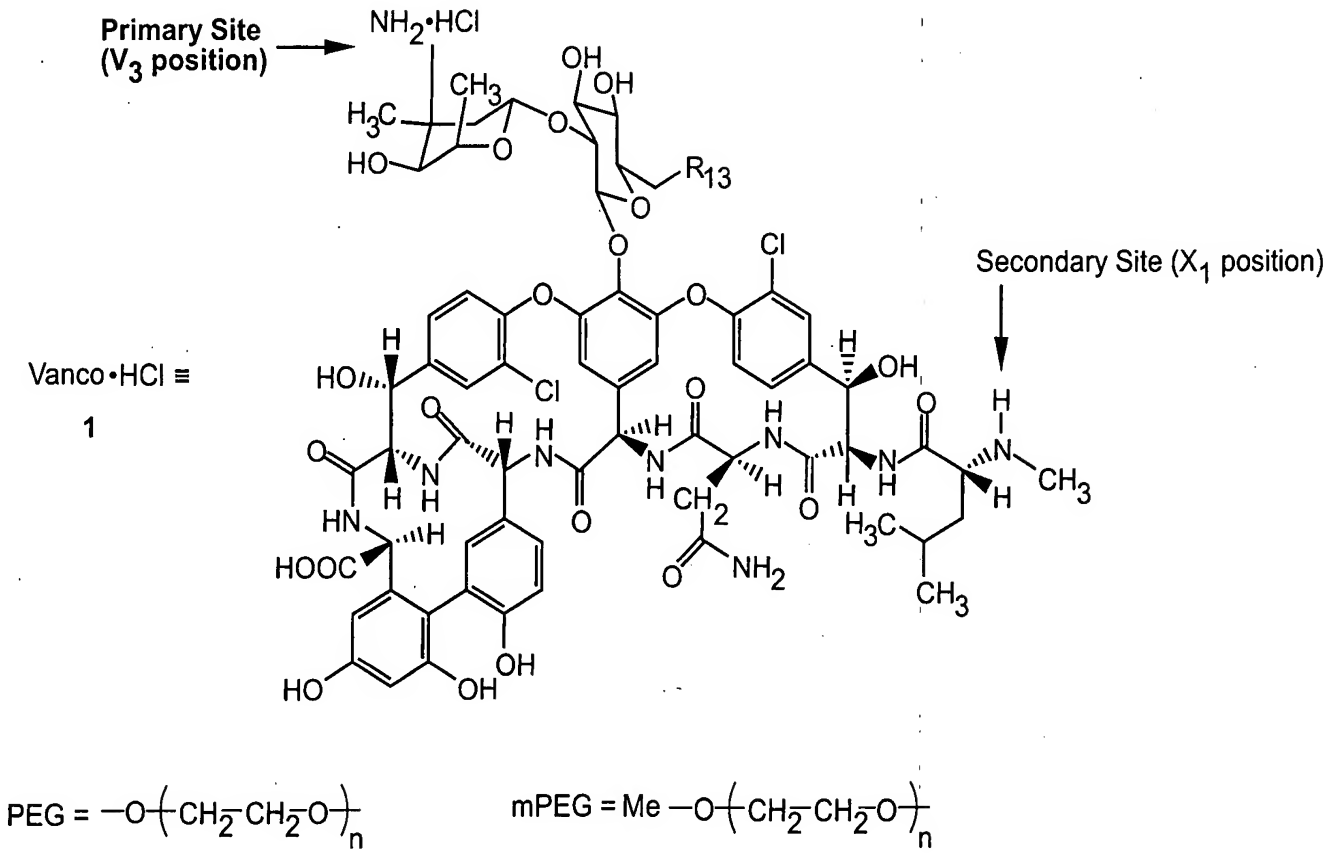
Primary Site
(V_3 position)
NH_2•HCl
Secondary Site (X_1 position)
Vanco•HCl ≡
1
PEG = $-O-(CH_2-CH_2-O)_n$
mPEG = Me $-O-(CH_2-CH_2-O)_n$

FIG. 1B

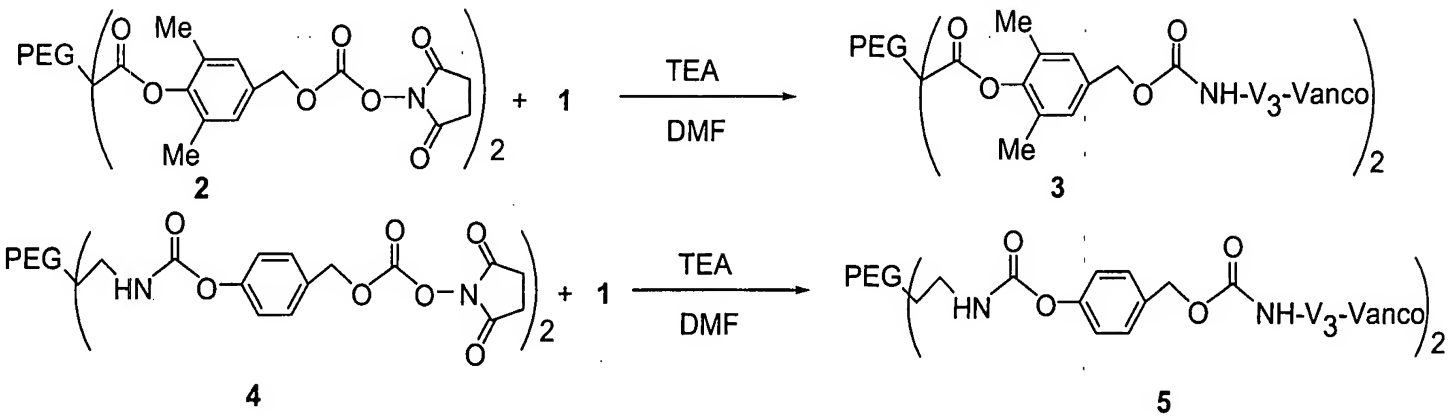

FIG. 2

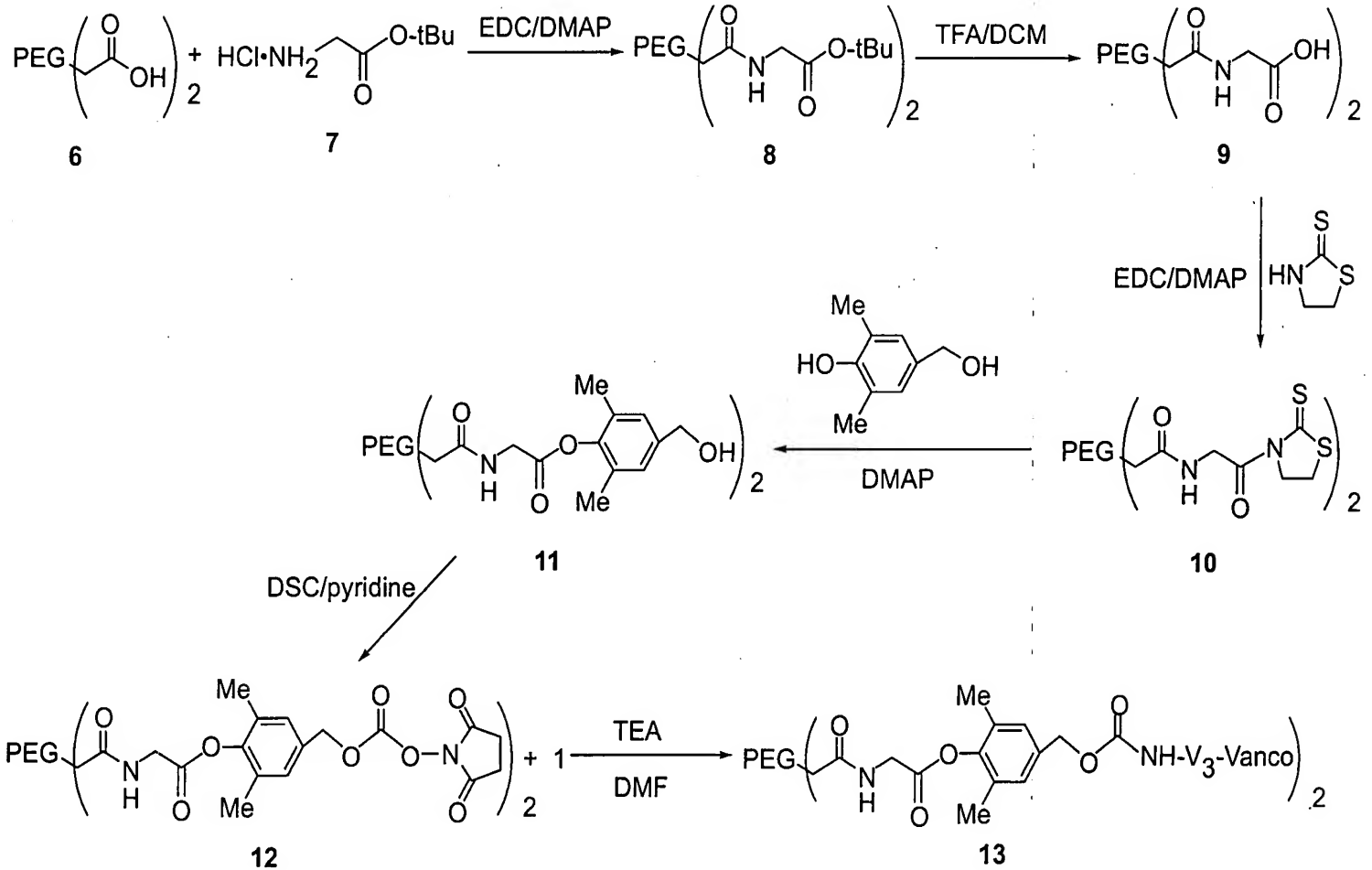
PEG
OH
2
HCl•NH2
O-tBu
EDC/DMAP
N
H
TFA/DCM
6
7
8
9
EDC/DMAP
HN
S
Me
HO
OH
DMAP
10
11
DSC/pyridine
12
TEA
DMF
1
NH-V3-Vanco
13

FIG. 3

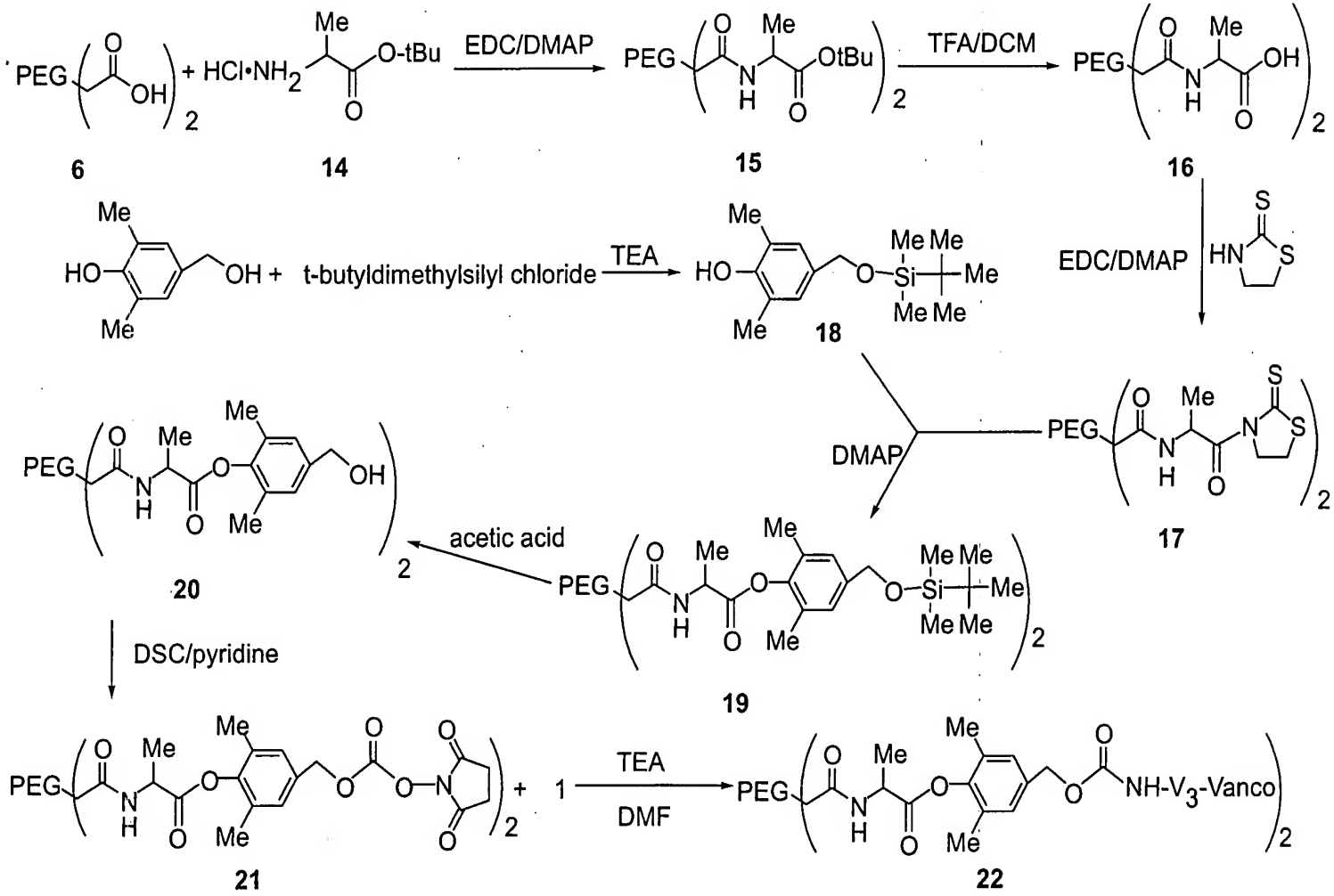
PEG
OH
2
+ HCl•NH2
Me
O-tBu
O
EDC/DMAP
OtBu
N
H
TFA/DCM
OH
6
14
15
16
HO
OH +
t-butyldimethylsilyl chloride
TEA
Me Me
Si
Me
18
EDC/DMAP
HN
S
17
DMAP
acetic acid
20
19
DSC/pyridine
21
TEA
DMF
NH-V3-Vanco
22

FIG. 4

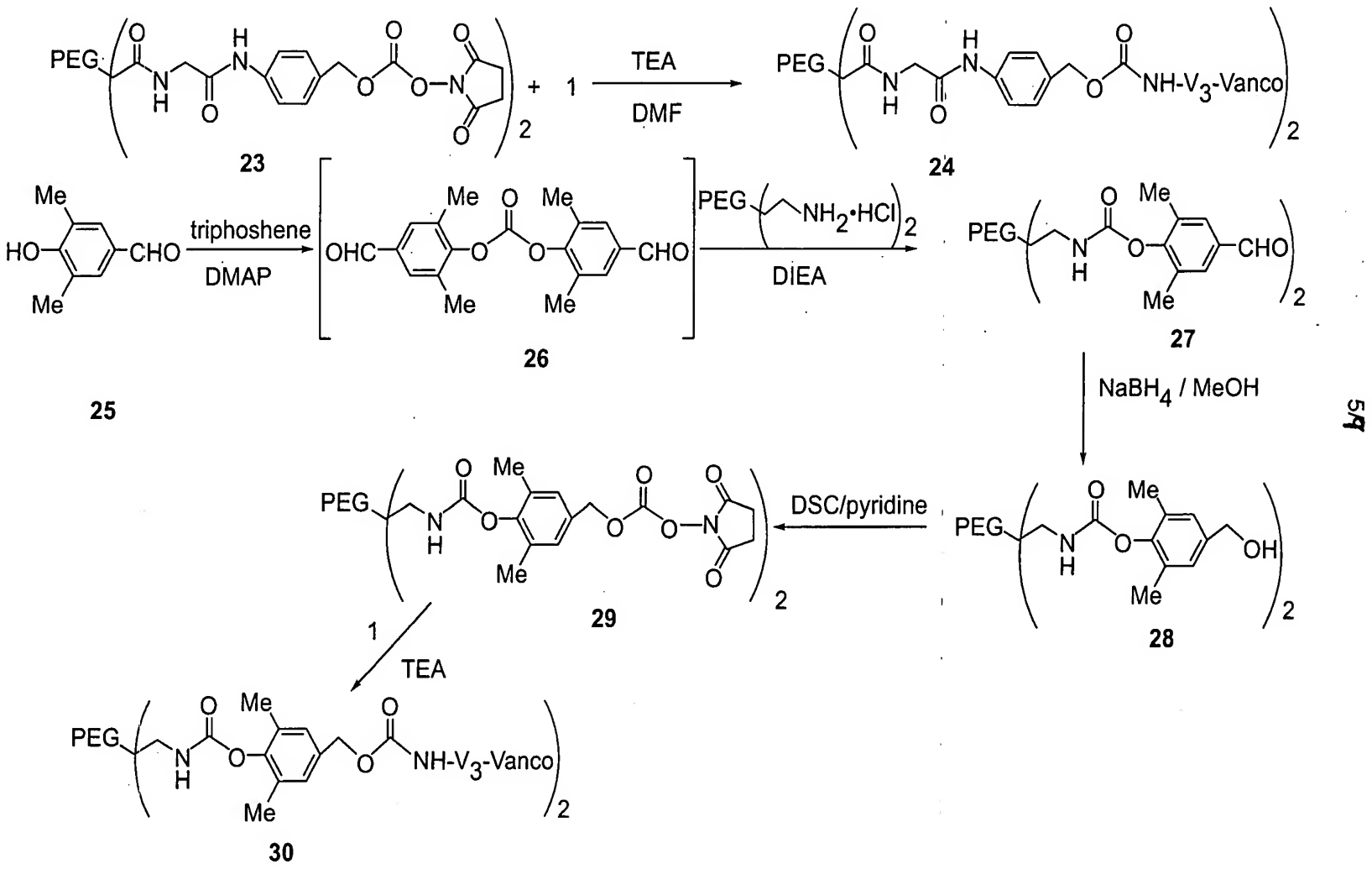
PEG
TEA
DMF
NH-V3-Vanco
23
24
triphoshene
DMAP
HO
CHO
Me
OHC
26
25
PEG
NH2•HCl
DIEA
27
NaBH4 / MeOH
DSC/pyridine
OH
28
29
1
TEA
30

FIG. 5

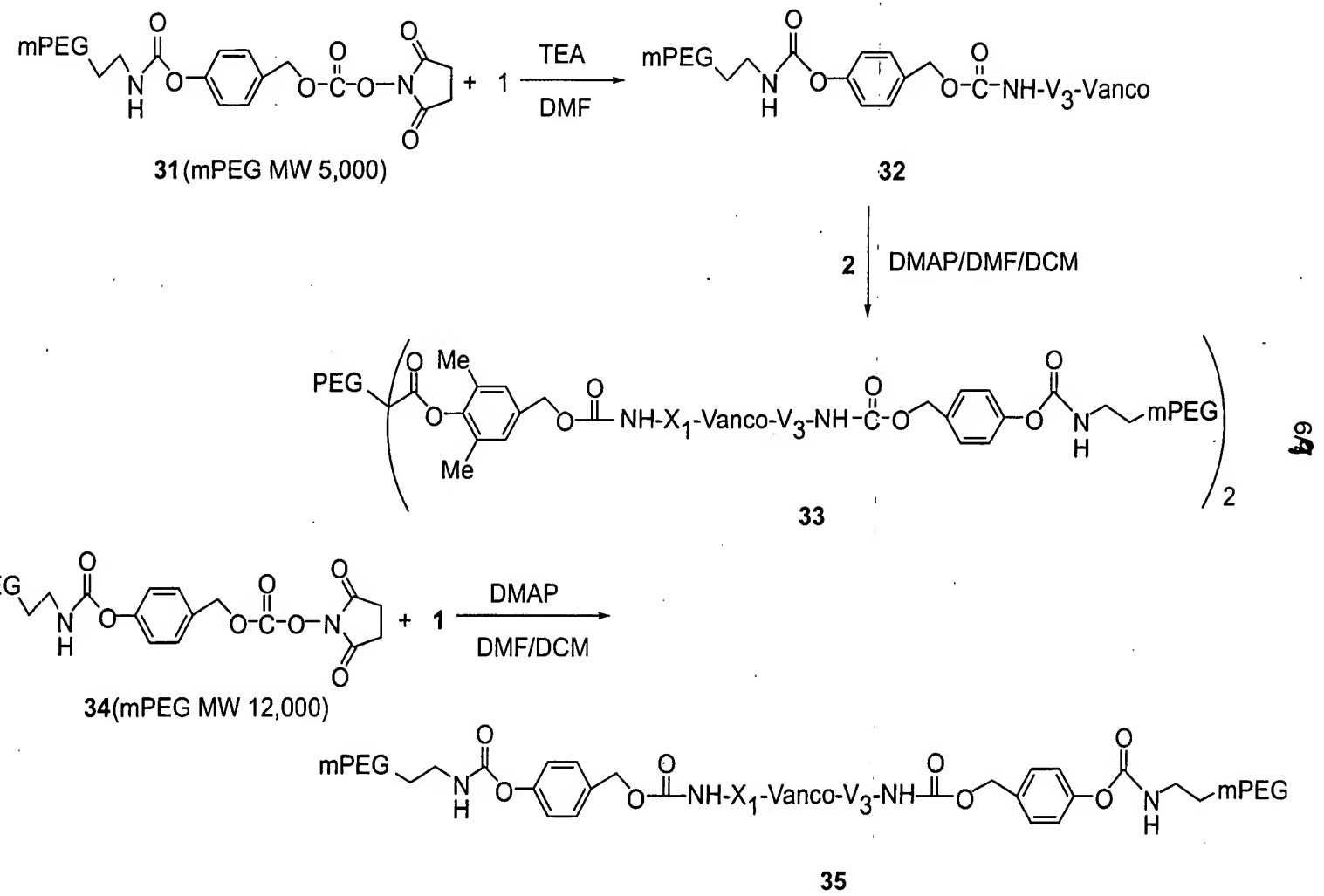
mPEG
TEA
DMF
+ 1
31 (mPEG MW 5,000)
32
V_3-Vanco
2
DMAP/DMF/DMF/DCM
PEG
Me
Me
X_1-Vanco-V_3-NH
mPEG
2
33
mPEG
DMAP
DMF/DCM
+ 1
34(mPEG MW 12,000)
mPEG
X_1-Vanco-V_3-NH
mPEG
35

Figure 6a.

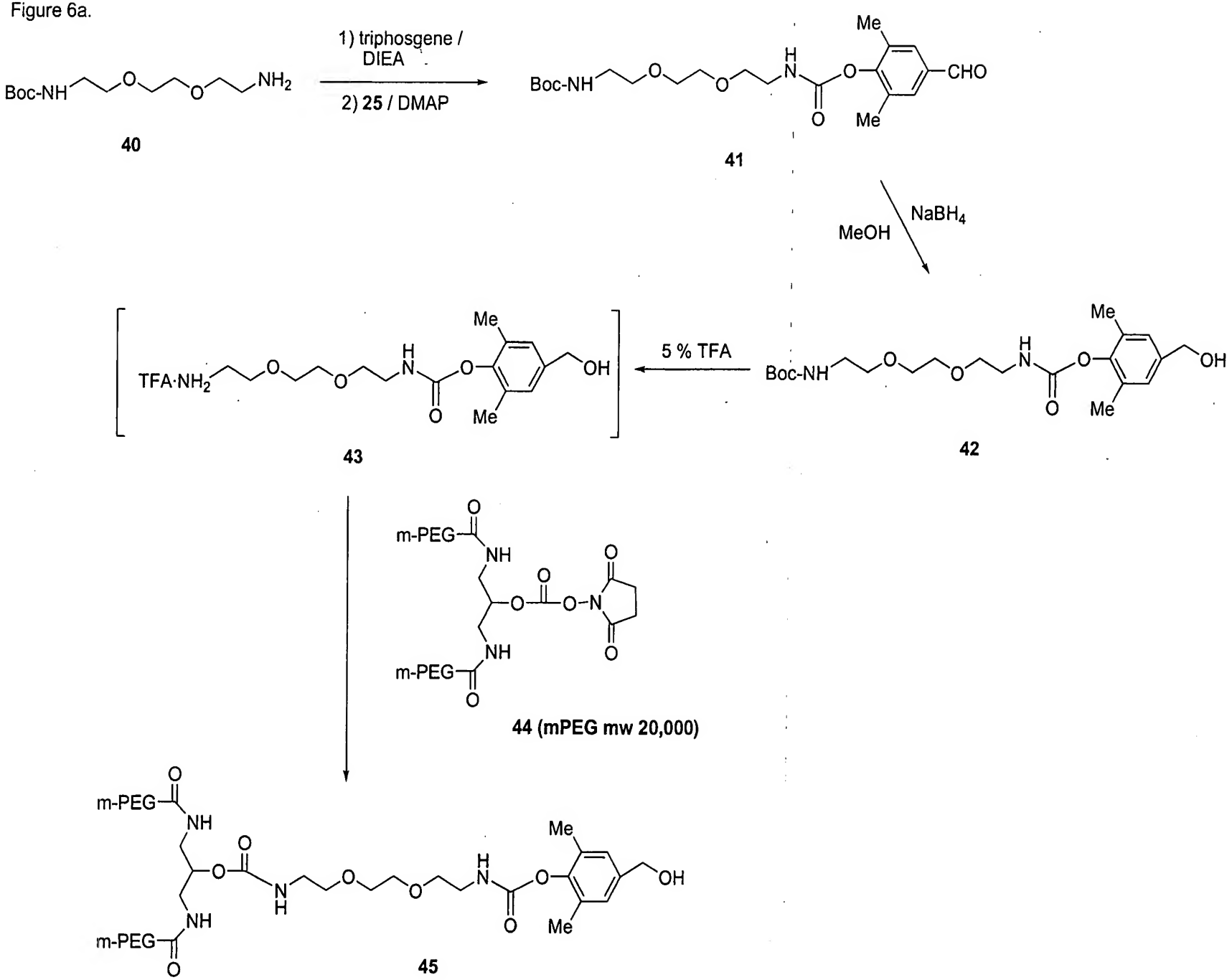
1) triphosgene / DIEA
2) 25 / DMAP
Boc-NH
NH2
40
CHO
41
MeOH
NaBH4
5 % TFA
TFA·NH2
OH
42
43
m-PEG
44 (mPEG mw 20,000)
45

Figure 6b.

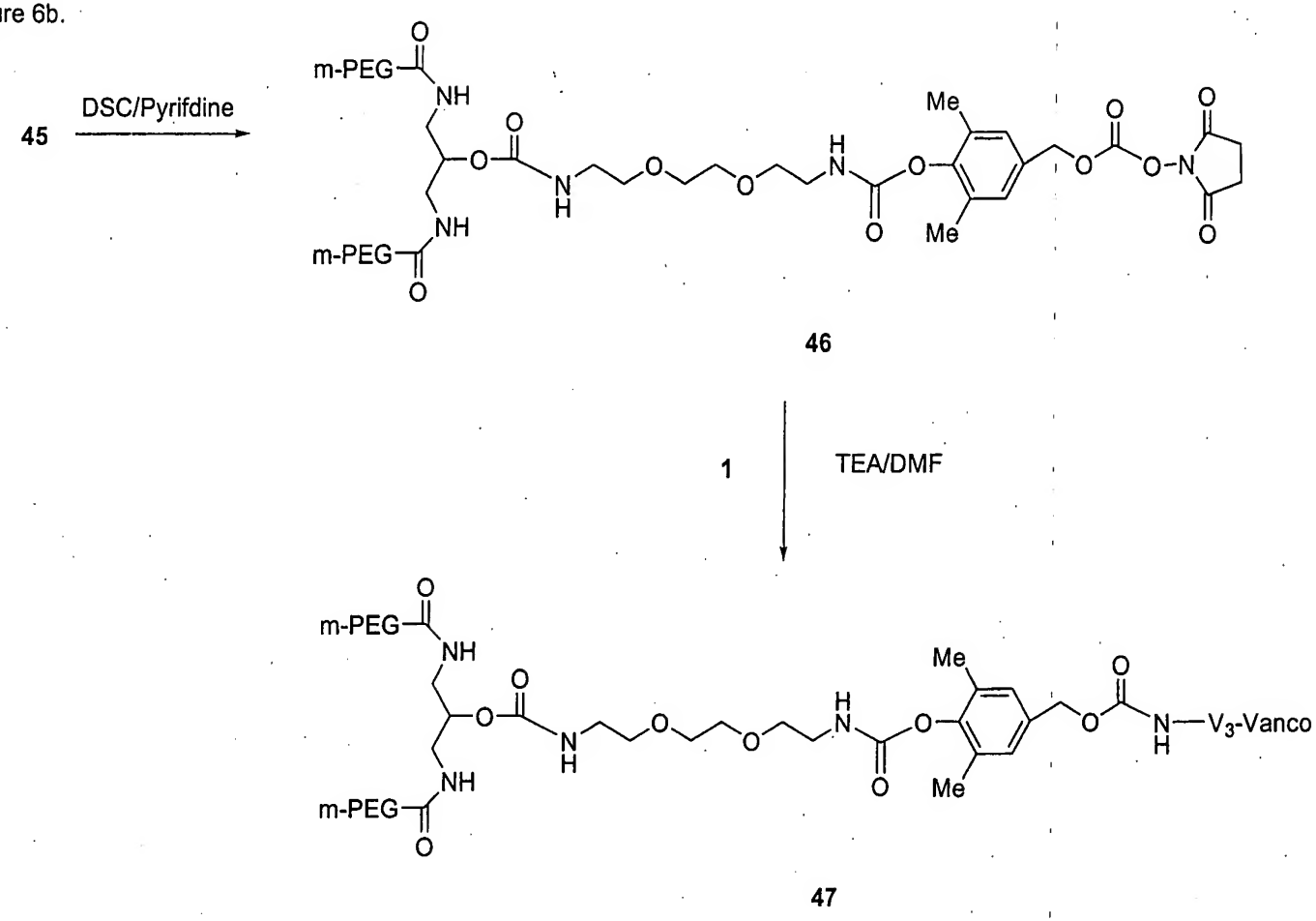

Figure 7.